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# CALORIMETRY OF A FLUID

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## ABSTRACT

In this paper a calorimetric method of determining the thermodynamic characteristics of a fluid is outlined. The basic principles involved and the application of the method to formulation of thermal properties for engineering uses are both analyzed. The method has been developed at the Bureau of Standards for determining the properties of steam.

A single calorimetric apparatus specially designed and with especial refinements provides a setting for a systematic group of experiments of four types in which four characteristic heat quantities are determined each as a function of temperature.

These experimental data provide a basis for formulation of the thermodynamic behavior of the fluid in terms of familiar and convenient properties within the limits of the observations.

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## I. INTRODUCTION

This paper presents the principles of a systematic method of observing the thermal behavior of fluids. The method is intended primarily for the purpose of obtaining data useful in heat engineering.

Certain characteristic thermodynamic properties of a fluid exhibit its behavior with respect to changes of temperature, pressure, volume, and energy. Knowledge of these properties is indispensable to engineers in analyzing problems which arise from the use of fluids in heat engines. It is customary to collect and arrange in the convenient form of numerical tables and graphical charts the values of these properties for fluids used as media in thermodynamic processes.

The most formidable problem in the preparation of a thermodynamic table or chart for a given substance is to obtain data adequate as to kind, range, and accuracy. With very few exceptions existing

thermodynamic tables have been prepared from scanty and incongruous data collected from various sources, and on that account require great dependence on the compiler's appraisal.

The discrepancies between steam tables bear witness to the difficulties of measuring thermodynamic properties and emphasize the need of further development of methods of measurement.

## II. CALORIMETRY AS A METHOD OF SURVEYING THERMAL BEHAVIOR OF A FLUID

Measurement of the amount of heat which enters or leaves a mass of fluid when its state changes affords a means of studying thermal behavior, appropriate for formulating those thermodynamic properties of a fluid which are important in engineering calculations.

Although calorimetry has been used for obtaining certain indispensable data, the full possibilities and advantages of this mode of experimental study as a systematic basis for a complete thermodynamic formulation have not been utilized. Formerly, when measurements of heat were made only in terms of the heat capacity of a chosen standard substance, such as water, when the technique of temperature control and measurement was only beginning to be developed, and when methods for controlling thermal leakage in calorimeters were yet crude, it was expedient to avoid where possible the inherent difficulties of calorimetric methods and use simpler and more easily manipulated means, such as the simultaneous observation of pressure, volume, and temperature, for establishing the thermal behavior of a fluid.

Development of trustworthy standards and methods for electrical measurements brought new possibilities to calorimetry both as to increased accuracy and enlarged scope. The adopting and perfecting of electric heaters, resistance thermometers, and thermocouples, have made it possible to develop calorimetry into a reliable agency for thermal research. Ways to confine heat within a definite region, in opposition to the inherent tendency of heat to dissipate, have been developed and it is now possible to refine the various elements of a calorimetric apparatus to such a degree that the measurements will be consistently accurate.

Conservation of energy is the keynote of calorimetry. One conception of a calorimeter is a place where we confine measured energy while observing the change in state which it produces in a measured sample of fluid.

If the sample is part liquid and part vapor the definite relation between saturation pressure and temperature makes it possible to keep a definite control on the state of the sample and to make it pass through definite processes which effectively exhibit its thermal characteristics.

The proposed method makes use of a single calorimetric equipment by means of which a system of measurements may be made which will determine some of the most essential thermodynamic properties of a fluid. In this method a sample of the fluid in a closed shell at some chosen temperature is heated electrically from the initial temperature and pressure to some other chosen state, or is withdrawn at any chosen temperature and pressure either as liquid or vapor. The energy input required for each of these processes is measured electrically. The

amount of heat added per unit mass in any of these processes is characteristic of the fluid and of the particular experimental process observed.

As the aggregate result of the group of measurements it turns out that the property of a fluid which is of utmost importance as a measure of available energy in a thermal process—that is, the "heat content" or "total heat"—is the one most directly determined by the several calorimetric processes, but that specific heat, entropy, and specific volume also may be determined from this group of measurements. The method has been developed at the Bureau of Standards, for determining the properties of steam, and has previously been described in part.<sup>1</sup> The analysis previously given, which was restricted to a saturated fluid, has been revised so as to make it more general, and now includes application of the method to determinations of properties of the superheated vapor.

In order better to visualize the physical aspect of the method, reference will be made to the actual apparatus which has been developed in collaboration with H. F. Stimson and E. F. Flock. This apparatus has been completed and has been used for a series of measurements extending over several years. Brief illustrated descriptions of general form of the apparatus, of some of the important details of construction, and of tentative experimental results obtained have appeared from time to time as progress reports.<sup>2</sup>

A comprehensive account of the construction, method of use, and results already obtained is now in preparation for publication. This account will contain the evidence as to the soundness of the method and the reliability of the results obtained. Only a very concise description of those vital features of the apparatus and procedure which pertain to the analysis of the method will be given here.

### III. DESCRIPTION OF EQUIPMENT AND EXPERIMENTS

#### 1. EQUIPMENT

The apparatus consists essentially of a calorimeter where a sample of water may be sufficiently isolated from other bodies to enable its amount, state, and energy to be accounted for. The sample may be made to pass through a chosen, accurately determined change of state while the accompanying gain or loss of heat is likewise accurately determined. The design of the apparatus provides for several such experimental processes selected for their physical simplicity and for their fitness and sufficiency to exhibit the thermal behavior of the fluid.

A quantity of water, part liquid and part vapor, is inclosed in a metal shell. The water is circulated rapidly about the interior in such a manner as to distribute heat and promote close approximation to thermal equilibrium. An electric heater continually bathed with flowing water provides a means of adding measured heat, which is speedily distributed throughout the calorimeter system. Outlets with valves provide for the introduction or withdrawal of either liquid or vapor. Detachable receivers suitable for weighing are connected to the outlets to hold the samples of water transferred.

<sup>1</sup> J. Opt. Soc. Am. & Rev. Sci. Inst., 8, No. 4, April, p. 519; 1924.

<sup>2</sup> Mech. Eng., 45, No. 3, p. 168; 1923; 46, No. 2, pp. 81, 83; 1924; 48, No. 11a, p. 808; 1924; 47, No. 2, p. 106; 1925; 48, No. 2, p. 152; 1926; 49, No. 2, p. 162; 1927; 50, No. 2, p. 152; 1928; 51, No. 2, p. 125; 1929; 52, No. 2, p. 127; 1930.

For confining the heat the calorimeter is well insulated from the influence of external sources of heat and cold. In operation, the temperature of an enveloping shell is kept very close to that of the calorimeter shell itself. The heat which passes by leakage to or from the calorimeter system is accounted for as a small correction which is determined. The power consumed in circulating the fluid and added to the system as heat is another small correction which is determined.

Means are provided for observing the following quantities:

(a) Température of the calorimeter and contents.

(b) Vapor pressure in the calorimeter.

(c) Mass of fluid contents of the calorimeter.

(d) Heat added to the system as electric power converted to heat and the small corrections for thermal leakage and circulation.

The apparatus is designed to permit four special types of experiments to be made. In the ideal case of perfect manipulation and control of experimental conditions these would consist essentially of the following processes:

1. Heating with fixed amount of contents.

2. Isothermal expansion by adding heat, evaporating liquid, and removing *saturated vapor*.

3. Isothermal expansion by adding heat, evaporating liquid, throttling, reheating, and removing *superheated vapor* at the saturation temperature and reduced pressure.

4. Isothermal expansion by adding heat, evaporating liquid, and removing *saturated liquid*.

## 2. HEAT-CAPACITY DETERMINATION

The experiment of the first type is a heat-capacity determination. In this experiment the temperature is raised from an initial to a final equilibrium value by adding heat, keeping the amount of fluid in the calorimeter constant. The pressure, the densities, and the relative proportions of vapor and liquid will change in the manner characteristic of the fluid. The volume of the container will change slightly with temperature and pressure. A single experiment of this type will determine the thermal capacity of the calorimeter and contents over the interval through which the state of the system is changed. This interval may be expressed in terms of either the temperature or the pressure, according to convenience. Two experiments of this kind, each extending over the same interval, but with different amounts of fluid in the calorimeter, will differ in observed thermal capacity by the thermal capacity of the difference in contents. Thus, the thermal capacity of the instrument may be eliminated and a value found for the thermal capacity of unit quantity of a definite combination of saturated liquid and vapor.

This result expresses a definite thermal property of the fluid, for its value is dependent only on the nature of the fluid and on the initial and final states. It bears a definite and simple relation to other more familiar thermal properties, particularly the change in heat content of the saturated liquid which it approximates in value and which is determined by this type of experiment supplemented only by experiments of type 4. An experiment of the first type is thus substantially a determination of the change in heat content of the saturated liquid. The resultant heat quantity differs from the change in heat content

by a correction term which is determined by the fourth type of experiment, and is small in amount at low temperatures, increasing with temperature and pressure.

### 3. LATENT HEAT DETERMINATION

An experiment of the second type is virtually a latent heat determination. In this experiment a definite portion of the contents of the calorimeter is withdrawn as saturated vapor at the calorimeter temperature, which is maintained approximately constant during the experiments by adding heat to compensate for the energy absorbed in evaporating the fluid. Such changes in the experimental conditions as do occur will be accidental deviations from the ideal constancy aimed at. These deviations can never be absolutely annulled, but their amount may be controlled by proper refinement of equipment and operation so that the effect is either negligible or else may be evaluated as a small correction.

The result of a single experiment of this type is a determination of the amount of heat which must be supplied when unit quantity of saturated vapor is removed from the calorimeter. This includes not only the quantity of heat required to evaporate the unit mass removed, but also the heat to produce an additional amount of vapor sufficient to fill the space which is vacated by the fluid withdrawn. The observed heat quantity differs from the latent heat of vaporization by this extra amount, and this correction turns out to be the same as that required to evaluate the heat content of the liquid from the result of the first type of experiment.

### 4. SUPERHEAT DETERMINATION

The third type of experiment is a measurement of the heat content of superheated vapor referred to that of saturated liquid at the same temperature. This experiment differs from the second by throttling the sample of vapor from the state of saturation to a lower pressure, leaving the temperature at which it is withdrawn the same as before. The second type of experiment is the limiting case where the throttling is zero and the change in heat content becomes equal to the latent heat of vaporization. A still more general type of experiment would be the case where fluid is withdrawn at any temperature and pressure which can actually be produced and observed. The special cases are simpler to deal with in actual experiments although the more general case is useful in developing the theory.

The throttling device consists of a closely fitting threaded metal plug at the entrance to the vapor outflow tube. Throttling occurs as leakage past this thread, and the degree of throttling or drop in pressure may be adjusted by advancing or withdrawing this plug. After passing the throttle the vapor enters a tube which is coiled within the vapor space of the calorimeter and leads to the outlet where the vapor is finally withdrawn from the calorimeter. The coiled tube between the throttle and the outlet is for reheating the vapor after reduction of pressure. The throttle and reheat tube are both situated in the vapor space where they are always bathed with saturated vapor. Condensation of saturated vapor on the tube supplies the heat necessary to bring the flowing vapor back to the saturation temperature

at which the calorimeter is being operated. The heat thus absorbed is a part of the total supplied to the calorimeter.

The whole process is equivalent to isothermal throttling of initially saturated vapor, effected in a place where any cooling which occurs in the process is automatically compensated without disturbing that uniform distribution of temperature which permits control and annulment of thermal leakage.

In this experiment the amount of heat is measured which must be supplied when unit quantity of vapor is produced by evaporation, reduced in pressure, and removed from the calorimeter at the saturation temperature which prevails within, where the evaporation takes place. This quantity of heat includes the latent heat of vaporization of unit mass, the correction for an extra amount evaporated to fill the vacated space, and the heat absorbed by the vapor in the process of isothermal throttling from saturation to the reduced pressure.

### 5. DETERMINATION OF CORRECTION

The fourth type of experiment determines the correction which is needed to reduce the results of the other three experiments to simpler terms. This correction is observed directly as the heat added to keep the system in equilibrium when a sample of saturated liquid is withdrawn, and is simply the heat required to vaporize enough liquid to fill the space vacated.

Further discussion of the physical interpretation of the results of the several types of calorimetric experiments will be reserved until after the quantitative relations have been analyzed. It will then become evident that the group of experimental processes each observed quantitatively over a range of experimental conditions, determines a group of thermal properties which, together with general thermodynamic relations and the two additional observed quantities, temperature and pressure, establish the thermal behavior of the fluid in a manner thoroughly consistent and suitable for practical formulation.

In actual experiments, slight departures from the ideal conditions of constant temperature, constant outflow, and constant energy input, will be bound to occur even with the most refined technique attainable. In order to take into account these fortuitous variations from the ideal processes the analysis will be developed first for the general case and then by proper specializations applied to the four particular experimental processes which are expected to be useful in practice.

## IV. ANALYSIS OF CALORIMETRIC PROCESSES

### 1. NOTATION

$M$  = Mass of fluid contents of calorimeter.

$\theta$  = Temperature on the thermodynamic scale.

$\pi$  = Saturation vapor pressure.

$V$  = Internal volume or capacity of calorimeter.

$u$  = Specific volume of saturated liquid.

$u'$  = Specific volume of saturated vapor.

$x$  = Fraction of fluid contents of calorimeter which is vapor. Quality factor.

$Q$  = Net heat added to calorimeter and contents in any experiment including electric power input, thermal leakage, and heat dissipated in work of circulating fluid.

$W$  = External work done by the system in any experiment.

$-dM$  = Any infinitesimal element of mass of fluid transferred from calorimeter.

$y$  = Fraction which is vapor of any infinitesimal element ( $-dM$ ) transferred.

$p$  = Pressure at which any infinitesimal element ( $-dM$ ) is transferred.

$v$  = Specific volume of fluid transferred.

$E_A$  = Internal energy of calorimeter.

$E_x$  = Internal energy of contents.

$\epsilon$  = Internal energy of unit mass of saturated liquid.

$\epsilon'$  = Internal energy of unit mass of saturated vapor.

$e$  = Internal energy per unit mass of fluid transferred.

$H$  = Heat content per unit mass of saturated liquid referred to the value at some arbitrary temperature as zero.  $H = \epsilon + \pi u$ .

$H'$  = Heat content per unit mass of saturated vapor referred to same zero as  $H$ .  $H' = \epsilon' + \pi u'$ .

$L$  = Heat of vaporization of unit mass of fluid.  $L = H' - H$ .

$h$  = Heat content per unit mass of fluid transferred, referred to same zero as  $H$ .  $h = e + pv$ .

$q$  = Heat added to unit mass of saturated liquid in a reversible process.

$q'$  = Heat added to unit mass of saturated vapor in a reversible process.

$\Phi$  = Entropy per unit mass of saturated liquid.

$\Phi'$  = Entropy per unit mass of saturated vapor.

$\phi$  = Entropy per unit mass of superheated vapor.

$\sigma$  = Specific heat of saturated liquid  $\frac{dq}{d\theta}$

$\sigma'$  = Specific heat of saturated vapor  $\frac{dq'}{d\theta}$

Subscripts 1 and 2 denote initial and final equilibrium values, respectively, of the quantities to which they are attached.

## 2. DERIVATION OF GENERAL EQUATION

The purpose of the analysis which follows is to formulate the relations between the quantities observed in the experiments and the properties of the fluid which are to be determined, with the ultimate object in mind of making a systematic formulation of the thermal behavior of the fluid in a convenient form. We shall briefly recall, of the things which happen in the experiment of the more comprehensive or general type, those changes or operations which directly concern the analysis.

A measured quantity of heat is added and distributed to the calorimeter and its fluid contents, part liquid and part vapor, and at the same time fluid is gradually withdrawn. These two actions are under the control of the operator. As a result a change occurs in the state of the calorimeter and the fluid within it. Accompanying this change of state, work is done on or by the system against external forces. The change in state is determined by suitable observation of the temperature and pressure, and these data, together with the observed data on the transfer of the fluid, gives a basis of accounting in terms of external work and internal energy for all the measured energy added in the form of heat. This accounting follows the principle of conservation of energy and is the first step in the analysis. The usual direction of the operations in an actual experiment is determined by convenience of electrically measuring heat into the system, and of measuring outflow of fluid, and by the direction of pressure change in throttling. Except for these practical limitations these operations are not limited in sense, and the analysis is not restricted to either direction.

We shall define the system to which the principle is to be applied as that space wherein by observation we may account for heat added, amount and state of matter, and work done. This definition is essentially a description of the calorimeter and its contents, a system which,

it is true, changes in mass, but for which, nevertheless, the energy account may be kept. In the present analysis we shall disregard as insignificant all changes of energy within the system other than measured heat added, external work done or change of internal energy, thus excluding changes in potential or kinetic energy of the aggregate mass. It then follows from the principle of conservation that whatever net energy is added to the system as heat, must appear either as net increase of internal energy of the system in its final state of equilibrium over that in its initial state, as net internal energy of fluid withdrawn, or as net work done against external forces, all these quantities being expressed in the same energy units. We may write this in our chosen notation

$$Q = [E_A]_1^2 + [E_x]_1^2 - \int_1^2 e \, dM + W \quad (1)$$

Since the various elements of internal energy appear in the present analysis only in intermediate steps where numerical evaluation is not required, it is not necessary yet to introduce a reference value, but it is sufficient to specify that all these elements of internal energy are referred to the same state as a datum.

This rudimentary equation will next be transformed into a form adapted to our purpose by introducing specifications as to the mass, volume, quality, and specific properties of the fluid.

In the first place the total volume,  $V$ , of contained fluid may be expressed in terms of its total mass,  $M$ , the quality factor or vapor fraction,  $x$ , and the specific volumes of the saturated vapor and liquid  $u'$  and  $u$  in the equation

$$V = Mxu' + M(1-x)u \quad (2)$$

Likewise the total internal energy,  $E_x$ , of the contained fluid may be expressed in terms of  $M$ ,  $x$ , and the internal energies of the saturated vapor and liquid,  $\epsilon'$  and  $\epsilon$  in the equation

$$E_x = Mx\epsilon' + M(1-x)\epsilon \quad (3)$$

Eliminating  $Mx$  from (3) by use of (2)

$$E_x = M\epsilon + (V - Mu) \frac{\epsilon' - \epsilon}{u' - u} \quad (4)$$

and since by definition  $H' = \epsilon' + \pi u'$  and  $H = \epsilon + \pi u$ , and also since  $H' - H = L$  we have

$$L = \epsilon' - \epsilon + \pi(u' - u) \quad (5)$$

whence we may eliminate  $\epsilon$  and  $\epsilon'$  in equation (4) and obtain

$$E_x = V \left( \frac{L}{u' - u} - \pi \right) + M \left( H - \frac{u}{u' - u} L \right) \quad (6)$$

Before substituting this value for  $E_x$  into equation (1) we will find a similar equivalent for  $[W]_1^2$ , the external work done by the system.

This consists of two possible parts, one the work done against the external pressure by reason of an increase in volume of the calorimeter shell, and the other the work done by the fluid as it issues from the calorimeter. The first part is the product of the constant and uniform external pressure by the increase of the external volume, and in all practical cases would be insignificant, particularly if the envelope space were evacuated for thermal insulation. The second part is the total work done by all the elements ( $-dm$ ) removed, each of which in emerging does a bit of work equal to the product of the instantaneous pressure,  $p$ , by the volume  $v(-dm)$  transferred. Neglecting the insignificant part, the whole work done by the system during an experiment is therefore

$$W = - \int_1^2 p v \, dm \quad (7)$$

Returning to equation (1) and substituting for  $E_x$  from (6), for  $W$  from (7), and  $h$  for  $e + pv$ , we have as the general equation—applying to all the processes to be considered

$$[Q]_1^2 = \left[ E_A - V\pi + \frac{V}{u' - u} L \right]_1^2 + \left[ M \left( H - \frac{u}{u' - u} L \right) \right]_1^2 - \int_1^2 h \, dM \quad (8)$$

### 3. REMARKS ON THE PHYSICAL INTERPRETATION OF THE GENERAL EQUATION

Equation (8) is an expression for the heat added in a complete experimental process of the general type which has been considered. It is now in convenient form for physical interpretation and for application to the special cases of the four types of experiment of the simpler kind, for the second member shows how the whole amount of heat added is disposed of, taking into account the quantity, distribution, state, and properties of the fluid, and the characteristics of the container. This equation properly applies to any process where heat is exchanged with a quantity of fluid consisting of part liquid and part vapor, as, for example, the operation of a boiler or a condenser, provided, of course, that we are able to keep the account of energy and material correctly. The main difference between our ideal calorimeter and a boiler consists in the refinements provided for accurate bookkeeping. The scale upon which a calorimeter is constructed, of course, need be only large enough for convenient construction and operation and accurate observation.

If we examine the individual terms of the second member of equation (8) we shall see that each of the three terms denotes a particular portion of the heat added, or its equivalent, very definitely identified with a particular part of the entire process.

The first term involves the internal volume and internal energy of the container itself but is independent of the amount of fluid contents, excepting that enough fluid must always be present to maintain the saturation condition. This term includes those characteristics of the calorimeter which affect the heat-absorbing capacity of the system. Neither of the other two terms refers to the calorimeter itself.

The second term expresses the heat added by virtue of the combined change in amount and state of the portion of fluid within the calorimeter between the beginning and the end of the experiment. This

term is entirely independent of the intermediate process by which this change takes place, being completely determined by the initial and final values of mass and temperature.

The third term completes the account by expressing the heat taken away from the system by the portion of fluid withdrawn. This term depends for its value not only on the initial and final states of the system, but upon the state of the issuing stream at every instant during the course of the experiment.

Inasmuch as the physical operations upon which equation (8) is based are indifferent as to direction, the equation is not limited in its application to changes in a particular sense. If, instead of an electric heating current, we should employ a current of cooling fluid in a coiled tube so that it could absorb and take out heat, the equation would still apply for a decrease instead of a rise in temperature, although the measurement of the heat would then have to be provided for in a different way. Also, except for the case of the throttling process, the transfer of fluid may occur either to or from the calorimeter without affecting the validity of the equation. Indeed it is possible even to apply it to a case where both directions of flow occur simultaneously, as, for instance, if we should introduce liquid and remove vapor at the same time, thus simulating the action of an ordinary steam boiler, or by reversing this process make the system operate as a condenser.

As far as theory is concerned, equation (8) is general in its application to the types of thermal processes which may take place in a saturated fluid, considered as an isolated system. We shall consider in detail the four specific types of experiments which are adapted to the determination of the thermal properties of the fluid.

#### 4. CONSTANT MASS EXPERIMENTS

In the first type of experiment the amount of fluid in the calorimeter is to be kept constant during a single experiment. For this condition, the last term in equation (8) vanishes. We will use the symbol

$Z$  to denote the quantity,  $E_A - V\pi + \frac{V}{u' - u}L$ . Let  $M_a$  and  $M_b$  denote the masses of the contents in two separate experiments in each of which the temperature of the calorimeter and contents is changed from  $\theta_1$  to  $\theta_2$ . Let  $Q_a$  and  $Q_b$  denote the measured quantities of heat added in the two experiments, thus obtaining the following two equations

$$Q_a = [Z]_1^2 + M_a \left[ H - \frac{u}{u' - u} L \right]_1^2 \quad (9)$$

$$Q_b = [Z]_1^2 + M_b \left[ H - \frac{u}{u' - u} L \right]_1^2 \quad (10)$$

Solving these two simultaneous equations for  $\left[ H - \frac{u}{u' - u} L \right]_1^2$

and  $[Z]_1^2$  we have

$$\left[ H - \frac{u}{u' - u} L \right]_1^2 = \frac{Q_b - Q_a}{M_b - M_a} \quad (11)$$

$$[Z]_1^2 = \frac{Q_b M_a - Q_a M_b}{M_a - M_b} \quad (12)$$

## 5. EVAPORATION EXPERIMENTS

In an experiment of type 2 saturated vapor is withdrawn from the calorimeter and consequently the  $h$  in equation (8) becomes  $H'$ . In order to take into account the effect of variations in the state of the vapor,  $H'$  may be separated into two parts, one a constant value,  $H'_1$ , and the other the deviation,  $H' - H'_1$ , from this constant value. If we substitute for  $h$ , these two values into equation (8) the last term, which expresses the energy transferred in the outflowing stream, may be divided, one portion corresponding to the value for outflow at the steady state corresponding to  $H'_1$ , and the other the effect of the variation of the state of the vapor from this ideal steady state. Making this substitution, also substituting  $Z$  for  $E_A - V\pi + \frac{V}{u' - u}L$  and expanding the expression  $\left[ M\left( H - \frac{u}{u' - u}L \right) \right]_1^2$  into the form

$$(M_2 - M_1) \left( H - \frac{u}{u' - u}L \right)_1 + M_2 \left[ H - \frac{u}{u' - u}L \right]_1^2$$

we have

$$Q = [Z]_1^2 + M_2 \left[ H - \frac{u}{u' - u}L \right]_1^2 + (M_2 - M_1) \left( H - \frac{u}{u' - u}L \right)_1 - (M_2 - M_1) H'_1 - L_1^2 \int_1^2 (H' - H'_1) dM \quad (13)$$

combining terms

$$Q = [Z]_1^2 + M_2 \left[ H - \frac{u}{u' - u}L \right]_1^2 + (M_2 - M_1) \left( L + \frac{u}{u' - u}L \right)_1 - \int_1^2 L_1^2 (H' - H'_1) dM \quad (14)$$

and solving for  $\left( L + \frac{u}{u' - u}L \right)_1$

$$\left( L + \frac{u}{u' - u}L \right)_1 = \frac{1}{M_2 - M_1} \left\{ -Q + [Z]_1^2 + M_2 \left[ H - \frac{u}{u' - u}L \right]_1^2 - \int_1^2 (H' - H'_1) dM \right\} \quad (15)$$

In equation (15) the quantities  $[Z]_1^2$  and  $\left[ H - \frac{u}{u' - u}L \right]_1^2$  would be determined from the results of experiments of type 1. As a matter of fact an experimenter would aim to keep conditions so steady that these two quantities would be negligible.

The quantity  $\int_1^2 (H' - H'_1) dM$  if large enough to be significant, would be determined by periodic observations of the state of the outflowing vapor during the experiment. By refinement of equipment and manipulation this correction as well as the two just previously mentioned would all be kept very small. The requirement to make

them all zero would be to maintain constant temperature and pressure, and for this ideal experimental condition we should have the simpler form of equation

$$\left( L + \frac{u}{u' - u} L \right)_1 = - \frac{1}{M_2 - M_1} Q \quad (16)$$

in which  $M_2$ ,  $M_1$ , and  $Q$  are determined by observation, thus allowing the quantity  $L + \frac{u}{u' - u} L$  to be determined at a certain chosen temperature in each experiment. This quantity is the property of the fluid, characteristic of this experiment, which was previously mentioned as being approximately the heat of vaporization at low temperatures and pressures where the ratio  $\frac{u}{u' - u}$  is small.

#### 6. THROTTLING EXPERIMENTS

In an experiment of type 3 superheated vapor is withdrawn at the temperature  $\theta$ , and the reduced pressure,  $p$ , and for this case the  $h$  in equation (8) may be denoted as  $(h)_{\theta p}$ . In a manner similar to that followed in the case of evaporation experiments,  $(h)_{\theta p}$  may be separated into a constant and a variable part; that is,

$$(h)_{\theta_1 p_1}, \text{ and } (h)_{\theta p} - (h)_{\theta_1 p_1}$$

but  $(h)_{\theta_1 p_1}$  is equal to  $H'_1 + [(h)_{\theta_1}]_{\pi_1}^{p_1}$

Substituting  $H'_1 + [(h)_{\theta_1}]_{\pi_1}^{p_1} + (h)_{\theta p} - (h)_{\theta_1 p_1}$  for  $h$  in equation (8), substituting  $Z$  for  $E_A - V\pi + \frac{V}{u' - u} L$ , and  $(M_2 - M_1) \left( H - \frac{u}{u' - u} L \right)_1 + M_2 \left[ H - \frac{u}{u' - u} L \right]_1^2$  for  $\left[ M \left( H - \frac{u}{u' - u} L \right) \right]_1^2$  as in the previous derivation of the special equation for evaporation experiments we have

$$Q = [Z]_1^2 + M_2 \left[ H - \frac{u}{u' - u} L \right]_1^2 + (M_2 - M_1) \left( H - \frac{u}{u' - u} L \right)_1 - (M_2 - M_1) H'_1 - (M_2 - M_1) [(h)_{\theta_1}]_{\pi_1}^{p_1} - \int_1^2 \{ (h)_{\theta p} - (h)_{\theta_1 p_1} \} dM \quad (17)$$

Combining terms

$$Q = [Z]_1^2 + M_2 \left[ H - \frac{u}{u' - u} L \right]_1^2 - (M_2 - M_1) \left[ (h)_{\theta p} - H + \frac{u}{u' - u} L \right]_1 - \int_1^2 \{ (h)_{\theta p} - (h)_{\theta_1 p_1} \} dM \quad (18)$$

and solving for  $\left[ (h)_{\theta p} + \frac{u}{u' - u} L \right]_1$

$$\left[ (h)_{\theta p} - H + \frac{u}{u' - u} L \right]_1 = \frac{1}{M_2 - M_1} \left[ -Q + [Z]_1^2 + M_2 \left[ H - \frac{u}{u' - u} L \right]_1^2 - \int_1^2 \{ (h)_{\theta p} - (h)_{\theta_1 p_1} \} dM \right] \quad (19)$$

The previous remarks about determining the values of the correction terms which account for the variability of experimental conditions apply to equation (19) as well as to equation (15), the only difference being that the last term in (19) accounts for whatever variation may occur in the state of the superheated vapor during the course of the experiment, and both temperature and pressure need to be specified, while in equation (15) the relation between temperature and pressure is definitely fixed for the saturated vapor. The simpler form of equation for the ideal experimental condition of constant temperature and pressure in the latter case would be

$$\left[ (h)_{\theta p} - H + \frac{u}{u' - u} L \right]_1 = - \frac{1}{M_2 - M_1} Q \quad (20)$$

in which  $M_2$ ,  $M_1$ , and  $Q$  are determined by observation, allowing the quantity  $(h)_{\theta p} - H + \frac{u}{u' - u} L$  to be determined at a certain chosen state.

This quantity differs from the characteristic property determined in the preceding experiment merely by the addition of the increase of heat content,  $(h)_{\theta p} - H'_1$ , which corresponds to the change in state produced by the throttling from the saturation state,  $\theta_1 \pi_1$ , to the state  $\theta_1 p_1$  at which the vapor leaves the calorimeter. The latent heat of vaporization, which is the change of heat content,  $H'_1 - H_1$ , for the constant pressure change of state from saturated liquid to saturated vapor is included in the result, and also the same factor or correction,  $\frac{u}{u' - u} L$ , for fluid evaporated which remains in the calorimeter. Except for this correction term the quantity measured with this calorimeter in a flow experiment is the increase in heat content for the entire change in state from the saturated liquid within the calorimeter to the state at which the fluid is withdrawn.

## 7. EXPERIMENTS IN WHICH SATURATED LIQUID IS WITHDRAWN

In an experiment of type 4, saturated liquid is removed from the calorimeter so that  $h$  in equation (8) becomes  $H$ .

In a similar manner as before we substitute  $H_1 + H - H_1$  for  $H$ ,

$$Z \text{ for } E_A - V \pi + \frac{V}{u' - u} L,$$

$$\text{and } (M_2 - M_1) \left( H - \frac{u}{u' - u} L \right)_1 + M_2 \left[ H - \frac{u}{u' - u} L \right]_1^2$$

$$\text{for } \left[ M \left( H - \frac{u}{u' - u} L \right) \right]_1^2$$

$$\text{and have } Q = [Z]_1^2 + M_2 \left[ H - \frac{u}{u' - u} L \right]_1^2 + (M_2 - M_1) \left( H - \frac{u}{u' - u} L \right)_1 \\ - (M_2 - M_1) H_1 - \int_1 (H - H_1) dM \quad (21)$$

Combining terms

$$Q = [Z]^2 + M_2 \left[ H - \frac{u}{u' - u} L \right]_1^2 - (M_2 - M_1) \left( \frac{u}{u' - u} L \right)_1 - \int_1^2 (H - H_1) dM \quad (22)$$

and solving for  $\left( \frac{u}{u' - u} L \right)_1$

$$\left( \frac{u}{u' - u} L \right)_1 = \frac{1}{M_2 - M_1} \left\{ -Q + [Z]^2 + M_2 \left[ H - \frac{u}{u' - u} L \right]_1^2 - \int_1^2 (H - H_1) dM \right\} \quad (23)$$

Again, as in the two previous cases, we have the three correction terms for variability of experimental conditions, two of which are determined from the results of separate experiments of type 1, and the last by periodic observations of the state of the issuing fluid.

The form of equation for ideally perfect operation of this type of experiment would be

$$\left( \frac{u}{u' - u} L \right)_1 = -\frac{1}{M_2 - M_1} Q \quad (24)$$

### 8. RÉSUMÉ OF THEORY OF EXPERIMENTS

As the result of a complete group of the four distinct types of experiments, each carried out as a series extending over the range of temperature and pressure within which the properties of the fluid are desired, we have four calorimetric quantities, each of which is characteristic of the process and of the particular fluid used, and each of which is completely determined with respect to the state of the fluid. We shall find it convenient to designate each of these four properties of the fluid by a symbol for use in formulating the intermediate steps by which other thermal properties are derived from these directly measured quantities. In addition to the four quantities which are calorimetric—that is, measured heat quantities—we may include the observed vapor pressure,  $\pi$ , thus making five experimental quantities, four of which are functions of temperature, while the other ( $\lambda$ ) is a function of temperature and pressure, as the basis from which to formulate the thermal behavior of the fluid. The definitions of these quantities are

$$\alpha = H - \frac{u}{u' - u} L \quad (25)$$

$$\gamma = L + \frac{u}{u' - u} L \quad (26)$$

$$\lambda = (h)_{\theta p} - H + \frac{u}{u' - u} L \quad (27)$$

$$\beta = \frac{u}{u' - u} L \quad (28)$$

It may be noted that  $\frac{u}{u'-u}$  is a pure ratio and  $L$  denotes the magnitude of a physical quantity which may be determined by experiment independently of any arbitrary choice of a zero datum. Hence the quantities  $\gamma$  and  $\beta$  may be evaluated at any chosen temperature without regard to any arbitrary datum. The quantity  $\alpha$  on the contrary contains the quantity  $H$  involving the internal energy of unit mass of the fluid which we are able to evaluate only with respect to some arbitrarily chosen reference value. Consequently the quantity denoted by the symbol  $\alpha$  can be determined experimentally only as a difference in value between two states of the liquid. The symbol  $\alpha$  is used with reference to the same arbitrary zero which is chosen for the quantity  $H$ , so that the same arbitrary constant is tacitly understood for both.

In the series of experiments the quantity  $\alpha$  referred to this zero may be determined either by measurement extending from the zero state to the various chosen temperatures throughout the range; or else by measurements of convenient intermediate increments of  $\alpha$ , which must cover the entire range.

The quantity  $\lambda$ , like  $\gamma$  and  $\beta$ , is determined experimentally at a definite state, the arbitrary constant being canceled when the difference between  $(h)_{\theta_p}$  and  $H$  is taken.

These five independently observed quantities when taken together with the thermodynamic relations which hold, in general, for all fluids, are sufficient to establish completely the thermodynamic properties of a fluid, over the range of conditions and to the accuracy determined by the experiments.

It will shortly be shown possible to deduce from these five directly measured thermal properties the other, more familiar thermal properties which are generally employed in dealing quantitatively with the thermodynamic processes of the fluid.

The completeness with which the whole system of thermal properties may be formulated from a group of data of this type is in practice limited by the experimental possibilities. The method can not be expected to be ideal in every particular, and the shortcomings must be watched for, not only in the preparations for experiments but in the formulation of results.

The employment of this group of independent experimental data, together with the necessary thermodynamic general relations, results in a formulation which is self-consistent.

The question of reliability of results is extremely important and in providing data for engineering purposes no opportunity should be overlooked to check the accuracy of results. This may be done in the first place by scrupulous attention to details of apparatus, manipulation observation, and calculation. In the second place, if possible, experimental results from different methods should be subjected to the test of mutual agreement with the general laws of thermodynamics.

The first four of the group of data—that is, the four calorimetric quantities—are characteristic thermal properties of a fluid, which have been employed here solely for the reason that they are useful in the experimental study of the fluid by the calorimetric method. We shall next outline a method by which the thermal behavior as

thus determined may be expressed in terms of the more fundamental properties as usually formulated for engineering calculations.

## V. OUTLINE OF METHOD OF FORMULATION OF DATA

The precise manner of evaluating and expressing as functions of temperature or pressure, or both, the various thermal properties which we may desire to formulate is a detail which may be handled in several ways.

There are three ways of exhibiting physical quantities in terms of independent variables, viz., empirical equations, graphs, and tables. Each of these has some virtue, but none is indispensable. It would probably be advantageous to express the properties of steam finally by all three methods as far as possible, but the process by which the data are thus formulated may depend to a considerable extent on the character of the data themselves and on the possibility of obtaining satisfactory empirical equations to represent the experimental facts. The process of formulation also should provide for the comparison of independent experimental data from different sources, and for the appraisal and adjustment of the numerical values to represent the best estimate of the truth.

We shall present here merely an outline of such a process which may be applied to the group of experimental data which we have recapitulated just above, resulting from the observations which may be made in the calorimeter specified.

By simple algebraic combination of equations (25), (26), (27), and (28) and without utilizing any further thermodynamic relations whatever, we may deduce the following group of equations

$$H = \alpha + \beta \quad (29)$$

$$H' = \alpha + \gamma \quad (30)$$

$$h = \alpha + \lambda \quad (31)$$

These three equations show how the four directly measured heat quantities,  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\lambda$ , determine the heat content of the fluid either as saturated liquid, saturated vapor, or as superheated vapor at any pressure below saturation in each case referred to the value at a chosen reference state.

It should be noted that these equations do not, in general, yield values of  $H$ , etc., as functions of temperature or temperature and pressure. They yield a value of  $H$ , for example, for every saturation temperature at which  $\alpha$  and  $\beta$  have been determined. Only in case  $\alpha$  and  $\beta$  are expressed as functions of temperatures will these equations lead to an equation for  $H$  as a function of temperature. Each of the quantities  $H$ ,  $H'$ ,  $h$  derived in this manner from the experimental data should be considered as denoting a series of values of that particular thermal property corresponding to the various chosen states of the fluid at which the observations have been made. If, therefore, the experiments have been suitably distributed as to temperature and pressure, we have thus the skeleton of a steam table, complete as far as heat content is concerned, which may be elaborated by interpolation, by graphical representation, or by formulation into an equation.

Thus heat content, perhaps the most vital of the thermal properties required in engineering calculations, is directly determined calorimetrically.

Owing to the fact that the type of calorimeter chosen for this method operates at the saturation limit, the range of the determination is continuous along the saturation limit and into the superheat region, thus bridging a gap which would otherwise need to be crossed by extrapolation.

The latent heat of vaporization equal to  $H' - H$ , is directly determined by the equation

$$L = \gamma - \beta \quad (32)$$

The ratio  $\frac{u'}{u}$  of the specific volumes of the saturated vapor and saturated liquid is determined by the equation

$$\frac{u'}{u} = \frac{\gamma}{\beta} \quad (33)$$

which results directly from equations (26) and (28).

To proceed further with the derivation of thermal properties from the group of experimental data it is necessary to use relations which depend on the second law of thermodynamics. We shall use the general relation

$$dh = \theta d\phi + vdp \quad (I)$$

which is a statement combining the substance of the first and second laws for a fluid subjected to a reversible change of state. We shall also use Clapeyron's equation

$$\frac{L}{u' - u} = \theta \frac{d\pi}{d\theta} \quad (II)$$

which is deducible from (I) for the special case of evaporation at a constant temperature.

It is, of course, necessary to have a knowledge of the zero of temperature on the thermodynamic scale relative to the working scale used in the measurements. Wherever temperature  $\theta$  appears as a factor it is to be referred to this absolute zero of temperature.

As a consequence of this last relation (II) it follows that

$$\frac{u}{u' - u} L = \theta u \frac{d\pi}{d\theta} \quad (III)$$

and therefore from equations (25), (28), and (26) that

$$\alpha = H - \theta u \frac{d\pi}{d\theta} \quad (34)$$

$$\beta = \theta u \frac{d\pi}{d\theta} \quad (35)$$

$$\gamma = \theta u' \frac{d\pi}{d\theta} \quad (36)$$

It will next be shown that the entropies of the saturated liquid and of the saturated vapor are determined by the calorimetric data  $\alpha$ ,  $\beta$ , and  $\gamma$  directly through these additional relations.

If we solve equation (I) for  $d\phi$  we have

$$d\phi = \frac{dh}{\theta} - \frac{v}{\theta} dp \quad (IV)$$

and since  $\frac{dh}{\theta} = d\left(\frac{h}{\theta}\right) + \frac{h}{\theta^2} d\theta$  we have by substituting in equation (IV)

$$d\phi = d\left(\frac{h}{\theta}\right) + \frac{h}{\theta^2} d\theta - \frac{v}{\theta} dp \quad (V)$$

and now applying this equation to saturated liquid, noting that  $h = H = \alpha + \beta$ , and  $v dp = u d\pi$

$$d\Phi = d\left(\frac{H}{\theta}\right) + \frac{\alpha}{\theta^2} d\theta + \frac{\beta}{\theta^2} d\theta - \frac{u}{\theta} d\pi \quad (37)$$

But by equation (35) the last two terms cancel so

$$d\Phi = d\left(\frac{H}{\theta}\right) + \frac{\alpha}{\theta^2} d\theta \quad (38)$$

and by integration of this equation

$$\Phi = \frac{H}{\theta} + \int \frac{\alpha}{\theta^2} d\theta + c \quad (39)$$

Applying equation (V) to the saturated vapor, noting that

$$\begin{aligned} h &= H' = \alpha + \gamma \text{ and } v dp = u' d\pi \\ d\Phi' &= d\left(\frac{H'}{\theta}\right) + \frac{\alpha}{\theta^2} d\theta + \frac{\gamma}{\theta^2} d\theta - \frac{u'}{\theta} d\pi \end{aligned} \quad (40)$$

But by equation (36) the last two terms cancel, so

$$d\Phi' = d\left(\frac{H'}{\theta}\right) + \frac{\alpha}{\theta^2} d\theta \quad (41)$$

and by integration

$$\Phi' = \frac{H'}{\theta} + \int \frac{\alpha}{\theta^2} d\theta + c \quad (42)$$

Equations (39) and (42) are suitable for calculation of the entropies of the saturated fluid from the calorimetric data. The first step—that is, calculation of  $H$  and  $H'$ —has already been indicated. The values of  $\frac{H}{\theta}$  and  $\frac{H'}{\theta}$  may be calculated directly. The term  $\int \frac{\alpha}{\theta^2} d\theta$  must be evaluated by taking account of how  $\alpha$  varies with temperature. An empirical equation for  $\frac{\alpha}{\theta^2}$  as a function of temperature would be a convenient means of evaluating this term, and for this purpose need only conform to the data in the range used, and be integrable. The constant  $c$  depends upon the arbitrary zeros chosen for the various quantities in the equation.

It has not been necessary to use vapor pressure,  $\pi$ , in any of the reductions this far for the properties of the saturated fluid, except incidentally perhaps as a means of taking account of slight variability in the experimental conditions. But if both temperature and pressure are observed simultaneously, either in this or other apparatus, an independent relation is obtained which with the calorimetric data determines the specific volumes of the saturated fluid. For this purpose use is made of equations (35) and (36), which are corollaries of Clapeyron's equation. Solving these equations for  $u$  and  $u'$  the specific volumes of saturated liquid and vapor, respectively, we have

$$u = \frac{\beta}{\theta} \frac{d\theta}{d\pi} \quad (43)$$

$$u' = \frac{\gamma}{\theta} \frac{d\theta}{d\pi} \quad (44)$$

These equations are suitable for calculating the specific volumes within the range where  $\frac{\beta}{\theta}$ ,  $\frac{\gamma}{\theta}$ , and  $\frac{d\theta}{d\pi}$  can be determined with the requisite accuracy.

The method of calculating the ordinary specific heat  $\sigma$  of the saturated liquid and  $\sigma'$  of the saturated vapor is merely another detail of mathematical derivation from the calorimetric data. If we define the specific heat of the saturated liquid as the rate of absorption of heat of the homogeneous saturated liquid, in place, relative to temperature rise—that is,  $\frac{dq}{d\theta}$ , denoted by the symbol  $\sigma$ —we may obtain the equation for  $\sigma'$  from equation (38) noting that  $dq = \theta d\phi$

$$dq = \theta d\left(\frac{H}{\theta}\right) + \frac{\alpha}{\theta} d\theta \quad (45)$$

whence

$$\sigma = \frac{dq}{d\theta} = \theta \frac{d}{d\theta} \left(\frac{H}{\theta}\right) + \frac{\alpha}{\theta} \quad (46)$$

and similarly for the vapor

$$\sigma' = \frac{dq'}{d\theta} = \theta \frac{d}{d\theta} \left(\frac{H'}{\theta}\right) + \frac{\alpha}{\theta} \quad (47)$$

For calculating the entropy of superheated vapor a simple method may be employed if the isothermal throttling experiments can in practice be so carried out that determinations of  $h$  are made at temperatures and pressures corresponding to intersections of suitable isothermals and constant pressure lines on the chart. From equation (I) at constant pressure

$$d\phi = \frac{dh}{\theta} \quad (48)$$

whence by integration

$$\phi = \int \frac{1}{\theta} \left( \frac{dh}{d\theta} \right)_p d\theta + c \quad (49)$$

For the specific volume in the superheat region, we have from equation (I) at constant temperature

$$v = \left( \frac{dh}{dp} \right)_\theta - \theta \left( \frac{d\phi}{dp} \right)_\theta \quad (50)$$

or, at constant entropy

$$v = \left( \frac{dh}{dp} \right)_\phi \quad (51)$$

It is evident that we may continue and calculate numerous other coefficients and derivatives representing certain thermal properties, such as specific heat at constant pressure, Joule Thomson effect, etc., for comparison with results of experimental data by other methods. It is not surprising, however, to find that there are practical limitations to the range within which some of the thermal properties may be determined by this method of measurement.

For example, it is obvious that high percentage accuracy would be impossible in determining the specific volume of the liquid at low temperature and pressure where both the measured heat quantity  $\beta$  and the rate of change of pressure with temperature  $\frac{d\pi}{d\theta}$  are very small, and the expression for specific volume,  $u$ , approaches the indeterminate form  $\frac{0}{0}$ . But fortunately this is a region where other methods of measurement are relatively easy and capable of great accuracy. On the other hand, as temperature and pressure increase, the magnitudes of the quantities which determine  $u$  by the calorimetric method get more favorable for accuracy, while other methods requiring actual measurement of volume are more formidable than at lower temperatures. Furthermore, the state of saturation in the calorimeter is a fundamental condition of the method. This constitutes an advantage in the determination of values of thermal properties at the boundary over methods which rely on extrapolation from observations confined to states in the superheat region.

In the case of approach to the critical state the fact that the properties of the liquid and vapor phases approach equality might be expected to make it more difficult to maintain perfect separation of the phases, thus giving rise to indeterminateness of the physical processes akin to the mathematical forms which thermal properties are supposed to exhibit in this region. It is certain that for steam the critical state would not be a favorable one for calorimetric measurements on account of the high values of temperature and pressure.

Aside from these limitations there is a range of conditions within which it is possible to determine by the proposed calorimetric method the numerical values of the thermal properties of a given fluid to an accuracy appropriate for engineering purposes. The calculation of these numerical values would not necessitate the setting up of an elaborate system of mutually consistent empirical equations. The values would nevertheless be consistent with thermodynamic criteria to the degree of accuracy fixed by the measurements and the calculations. The thermodynamic criteria will have been already included as independent relations used in the scheme of calculating the several properties from the group of independent experimental quantities.

We have, in what has gone before, the skeleton of a formulation of the thermal behavior of the fluid. The formulation may be exhibited in either of the three ways previously pointed out. The numerical values may be tabulated, interpolating by the usual methods between the determined points. They may be plotted graphically in a variety of ways. They may be used to determine the constants in a series of empirical formulas. Or any combination of the three methods may be used. The details of the precise manner of formulating the data for actual use in thermodynamic calculations is beyond the scope of this paper which merely aims to establish the basic principles of one method of determining the thermal behavior of a fluid.

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